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Canada Centre for Mineral and Energy Technology | Centre canadien de la technologie des minéraux et de l'énergie

IRON REMOVAL FROM FERROUS CHLORIDE LEACH LIQUORS

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by

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ABSTRACT

Iron removal was briefly studied for a chloride process stream containing approximately 55 g/L iron, 175 g/L NaCl, 8 g/L lead, and 4 g/L zinc. Up to 15 g/L of iron was removed from the stream by oxidation with oxygen gas at atmospheric pressure and 90°C in a highly agitated reaction kettle after 6 hours of operation. Removal of up to 44 g/L after 6 hours was attained by controlling the solution pH with CaO. Sulphate addition in the form of $CaSO_4$ yielded a jarosite product of improved filterability that contained 0.5 weight % lead. Zinc was not incorporated into the precipitates.

ÉLIMINATION DU FER DES SOLUTIONS DE LIXIVIATION DE CHLORURE FERREUX

par

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RÉSUMÉ

L'élimination du fer a fait l'objet d'une brève étude lors de l'essai d'un circuit de chlorure contenant approximativement 55 g/L de fer, 175 g/L de NaCl, 8 g/L de plomb et 4 g/L de zinc. Après six heures de marche, jusqu'à 15 g/L de fer ont été éliminés du cycle par oxydation avec de l'oxygène à la pression atmosphérique et à une température de 90°C au moyen d'une installation comportant une chaudière très agitée. Il a été possible d'éliminer jusqu'à 44 g/L de fer après six heures de marche en réduisant le pH de la solution avec du CaO. L'addition de sulphate sous forme de $CaSO_4$ a donné un produit de jarosite dont la filtrabilité était améliorée et qui avait une teneur en plomb de 0,5 % en poids. Les précipités ne contenaient pas de zinc.

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INTRODUCTION

CANMET's flowsheet for the leaching of a complex Zn-Pb-Cu-Ag sulphide ore from New Brunswick is shown in Fig. 1 (1,2). Ferric chloride is employed to leach metal values from the ores in two stages. Conditions are arranged so that the leach liquor coming out of the first stage is in a reduced condition, which facilitates the removal of the metals via copper-silver cementation, lead crystalization, and zinc solvent extraction. The current paper is concerned with an iron removal step prior to chlorination of the stream and its return to the second stage leach. While most of the iron in the concentrate remains as relatively insoluble sulphides, about 5 g/L of iron is added to the leach liquor during extraction. In order to properly control leaching conditions, it is desirable to maintain the iron concentration in solution at about 50 g/L.

Two iron removal options were considered in this study: the removal of about 5 g/L from the total stream (without adding reagents other than oxygen); and the treatment of a bleed stream from which 50% of the iron would be removed. A process at atmospheric pressure that would yield a filterable product with acceptable metal losses (Pb, Zn) was sought. Efforts were restricted to the use of oxygen gas and air as oxidants, due to their lower cost when compared with that of other oxidants such as H_2O_2 etc.

LITERATURE SURVEY- OXIDATION

The oxidation of ferrous ions to ferric ions in sulphate and chloride media by oxygen gas occurs according to the overall equation (3,4).

$$2Fe^{2+} + 2H^+ + 1/2O_2 \rightarrow 2Fe^{3+} + H_2O \qquad (1)$$

The rate of the reaction is dependent on the temperature, the nature of the solution (concentrations of Fe(II), H^+, NaCl, and O_2) and mass transfer between the gaseous and liquid phases. Sufficiently high agitation is required to minimize the mass transfer resistance (5). The reaction has been found to be of order 1 to 2 with respect to the Fe(II) concentration, depending on the solution conditions (concentrations of HCl, $FeCl_2$, and

NaCl), experimental technique, and manner of interpretation of the results by various workers (4,5,6,7,8,9,10,11). The consensus is that the reaction is first order with respect to the oxygen partial pressure. Tables 1a and 1b show proposed reaction mechanisms for the first and second order rate expressions. Several variants may be found in the literature (3,11,12).

It has been suggested (4) that the discrepancy in the results of different workers can be explained when the activity of HCl (a_{HCl}) is used in rate expressions. High ionic strengths in a chloride medium result in very large activity coefficients for H^+ and Cl^-. This is readily seen in Table 2 (13). With that addition, the rate model over a fairly wide range of conditions may be expressed as:

$$\text{rate} = \frac{d}{dt}[Fe(II)] = -k.a_{HCl}.[Fe(II)]\ pO_2 \qquad (2)$$

which is first order with respect to HCl, Fe(II), and O_2, or third order overall.

Atmospheric oxidations are typically carried out between 85 and 90°C. Higher temperatures increase the rate of the oxidation reaction (which is slow at room temperature), but the overall rates decrease above 90°C, probably due to decreased solubility of oxygen in solution at the higher temperatures (14). Two catalysts for the oxidation of ferrous iron often mentioned in the literature are Cu^{2+} and activated carbon (15).

LITERATURE SURVEY- PRECIPITATION OF IRON

There are three major precipates that are useful means of removing iron from acidic chloride solutions: jarosite, goethite/akageneite, and hematite.

Jarosite (a possible balanced equation for Na jarosite)

$$Na^+ + 3Fe^{3+} + 2SO_4^{2-} + 6H_2O \rightarrow NaFe_3(SO_4)_2(OH)_6 + 6H^+ \qquad (3)$$

Goethite/Akageneite (7,16)

$$Fe^{3+} + 2H_2O \rightarrow FeOOH + H^+ \quad (4)$$

$$6FeCl_2 + 3/2\ O_2 + H_2O \rightarrow 2FeOOH + 4FeCl_3 \quad (5)$$

Hematite (17)

$$12FeCl_2 + 3O_2 \rightarrow 2Fe_2O_3 + 8FeCl_3 \quad (6)$$

$$2FeCl_3 + 3H_2O \rightarrow 2Fe_2O_3 + 6HCl \quad (7)$$

Table 3 (18) summarizes the conditions required for the formation of each of these products. Goethite and jarosite will form at atmospheric pressure and moderate temperatures. Appreciable rates of formation of hematite require higher temperatures and pressures. Jarosite formation requires the presence of sulphate in solution (10 g/L (16)), has a lower "product purity" than either goethite or hematite, and will tend to break down into the thermodynamically more stable goethite at higher pH's (such as would result from rainfall in a tailings pond), with sulphuric acid as a byproduct. On the other hand, kinetics favor the formation of jarosite over the formation of goethite, and the jarosite will form at lower pH's. All three products have good filtration characteristics, especially when compared with iron hydroxide ($Fe(OH)_3$) which forms above about pH 2 (3), depending on solution conditions. The filterability of goethite formed in zinc sulphate processes decreases as the pH rises above 2.5 (19).

Ni, Co, Cu, Zn, and Mn are entrained with goethite precipitate through cationic sorption (18). These impurities can amount to 0.2 to 3 weight % of the precipitate. Both SO_4 (3-15%) and Cl (0.5 to 7%) are also incorporated in the product. Besides the simple alkali jarosites indicated in Table 3, both plumbojarosite and argentojarosite may be formed (20,21,22). The alkali jarosites are, however, preferentially formed where both alkali cations and lead are present in solution, reducing the lead content from 12 to 16% in a typical plumbojarosite to 1 to 2%. In sulphate media, silver and alkali jarosites form nearly ideal solid solutions and much of the silver present in solution may be lost to the jarosite precipitate. In concentrated chloride media the silver forms $AgCl_2^-$ and

$AgCl_3^{=}$ complexes, and only 0.1% of the silver is lost to jarosite. Divalent metals (Cu^{2+}, Zn^{2+}, Co^{2+}, Ni^{2+}, Mn^{2+}, and Cd^{2+}) may be incorporated into the jarosite through substitution for iron, accounting for up to 1 to 4% of the jarosite product.

There are a number of commercial processes used for the elimination of iron from hydrometallurgical streams (16). The US Bureau of Mines, Cominco, Minemet and Duval processes are summarized in Table 4. Note that these processes involve streams with appreciable amounts of copper.

EQUIPMENT AND PROCEDURE

Two kilograms of solution were contacted with oxygen gas in a 2 litre glass reaction kettle. The temperature was maintained at a constant value either by the use of an electric heating jacket or by immersing the reaction kettle in a silicon oil constant temperature bath. A 3.8 cm diameter three-bladed polyethylene marine impellor spinning at 1500 rpm provided agitation. Baffles were not used during these experiments. Instead, vortex formation and gas entrainment were promoted, which resulted in a gas-liquid interfacial area that was somewhat independent of the gas flowrate. (However, the gas dispersion tube, thermometer, and pH probe provided some baffling.) A vapor condenser reduced losses by evaporation. Oxygen or air were introduced into the bottom of the reaction kettle by an open ended 3/16" polyethylene tube that extended down through the solution. Gas dispersion tubes were not used as they rapidly plugged up with precipitate. The gas flowrate was monitored by a flowmeter.

Twenty-five mL samples were withdrawn six times during the course of the oxidations. The samples were weighed and immmediately filtered. The filtrate was retained in an unmodified form for analysis after determining its emf. The precipitate was washed with 20 mL of 1M NaCl, and twice with 20 mL of distilled water. At the end of the runs the entire slurry was treated in a similar fashion. In some of the runs the precipitate "redissolved" when washed with H_2O, so a 3M NaCl wash was employed. Precipitates were dried at 125°C for 16 hours.

Table 5 shows the analysis of the ferrous chloride liquors that were used in the experiments. Table 6 summarizes the conditions for each oxidation run. Runs 1 to 3 provided preliminary data about the process as well as the effect of temperature. Based on the results of these runs and those of reference (7), a temperature of 90°C was selected for the remaining runs. Changes in the remaining experiments were related to oxygen partial pressures, sulphate concentrations, and pH control. The oxygen partial pressure was lowered in two of the runs by using air instead of oxygen. Sulphate levels depended on whether a low sulphate or high sulphate liquor was used. The sulphate level was also increased in some of the runs by the addition of $CaSO_4$ or $NaSO_4$. CaO and HCl were utilized in runs requiring pH control. During the pH controlled runs, a pH electrode was left in the solution for the course of the run, reagents being added periodically by hand in order to readjust the pH.

Figure 2 shows the activity of the hydrogen ion (10^{-pH}) as a function of the concentration of HCl in a 3 molar NaCl solution. A literature value is also shown in the figure. The activities were measured by a standard glass pH combination electrode. The measured activity of 1.0 molar for an HCl concentration of 0.5 molar is within 10% of the literature value of 1.1 molar. The slope of the line indicates a near constant activity coefficient of 2.

RESULTS

Iron removal of up to 15 g/L after 6 hours of operation was attained in runs to which no reagents other than oxygen were added. When the pH was maintained at 1.3 by the addition of CaO, up to 44 g/L of iron was removed after 6 hours. In comparison to the initial iron of 55 g/L, these results correspond to 27% and 80% iron removal respectively.

Table A-1 in the appendix contains processed data for the experimental runs. The total iron and ferrous ion concentrations were analyzed directly. The rate data for oxidation and precipitation were calculated by measuring the slopes of curves drawn through data points with a french curve. These rate data contain substantial error arising from the interpretation or judgement involved in drawing the smooth curves. Not all

solutions were analysed for sulphate, so calculated sulphate concentrations (based on a sulphur mass balance) are included as well as the measured values. The reported values of the iron in precipitates are based on the iron mass balance. These calculations agreed very well (within 5 to 10%) with calculations based on the mass of precipitate and its iron content.

Typical trends of the solution pH and emf during the course of a run are shown in Figures 3 and 4. The emf increased smoothly for all runs. In the absence of pH controls, the pH rose rapidly to a maximum within the first hour, thereafter declining gradually. Figures 3 and 4 illustrate the reproducibility of the experimental results, as run 15 was a duplicate of run 12, while run 6 was similar to run 2 (a slighly lower oxygen flowrate was used in run 6). Runs 15 and 12 gave almost identical results for solution pH, emf, and the amount of solid precipitate, thereby suggesting that the results are reproducible. However, some variations might be present in the results of other runs due to specific problems such as the control of the gas flowrate and the exact positioning of the impellor (which is what happened in run 6, intended as a duplicate of run 2).

The solution emf could be relied on as a rough guide to the per cent of ferric ion in solution (see the correlation of experimental data in Figure 5). However, the percentage of ferric ion in solution was not a good indication of the extent of oxidation nor of the extent of precipitation. Rather, it is the net effect of oxidation and precipitation because ferric ion is produced by oxidation and consumed by precipitation.

THE EFFECT OF TEMPERATURE

An operating temperature of 90°C was chosen for this project based on the results of the first three runs (Figures 6a and 6b). The oxidation and precipitation of iron was markedly better at 90°C than at either 80°C or 100°C.

GAS FLOWRATES

In spite of the great excesses of oxygen available for the oxidation and precipitation of iron, the gas flowrate had an important influence on both processes as shown in Figure 7. This may be due to the enhanced liquid-gas surface area resulting from higher gas feedrates, in spite of the attempt to maintain near constant surface areas by the use of

vortexing. Thus, mass transfer limitations could have affected the results of the experiments, but this point cannot be verified by the present data, as all "normal" runs were carried out at the highest gas flow.

OXYGEN PARTIAL PRESSURE

Figure 8 shows that the increased partial pressure of oxygen in a pure oxygen gas stream as compared to an air stream resulted in an increase in the rate of oxidation. The rate of precipitation was also greater for runs using oxygen gas. The increased rate of oxidation is in accordance with Equation 2.

pH CONTROL

Three runs were carried out at constant pH levels (with the low sulphate liquor). They are shown in Figure 9 alongside data for run 12 for which the pH was not controlled. It appears that the rate of oxidation is slightly reduced by decreasing pH (in contrast to the predictions of Equation 2), although the difference is not great and may be due to expe imental error. This would imply that increasing H^+ concentrations inhibit the oxidation process but only marginally so, as the rates are similar in spite of the almost tenfold difference in hydrogen ion concentration. In contrast to its lack of effect on the oxidation process, the solution pH is very important to the precipitation processes. As shown in Figure 9b, increased pH accelerates the precipitation of iron. In run 18 the pH was maintained at a comparatively low value of 0.5, which prevented any precipitate from forming.

SULPHATE LEVELS

As illustrated in Figure 10a, the level of sulphate present in the solutions did not appreciably affect the oxidation of ferrous complexes nor did it have much effect on precipitation as shown in Figure 10b (although run 8, with a very high sulphate concentration, yielded more precipitate than the other runs). But whereas the rate of precipitation was not greatly dependent on sulphate levels, the nature of the precipitate certainly was.

THE NATURE OF THE SOLID PRECIPITATES

X-ray diffraction revealed that precipitates from the high sulphate liquor were primarily $NaFe_3(SO_4)_2(OH)_6$ (sodium jarosite), with some akageneite (β FeOOH). The chemical analysis of the precipitates indicated that roughly 80 to 90% of the precipitate was jarosite when appreciable amounts of sulphate were present. The jarosite product was easier to filter than the other types of precipitates that were obtained. When dried, jarosite easily crumbled to a powder, while precipitates of a predominantly akageneite nature were hard and difficult to break. When filtering the akageneite precipitates, the filter cake cracked, while the jarosite filter cakes remained whole and easily washable. In runs 19 and 22 a different type of precipitate formed that had a tendency to break down when washed with distilled water, passing easily through Whatman number 3 filter paper (medium speed paper). Both of these runs used low sulphate liquor, and did not receive other sources of sulphate. The precipitate thus formed was very difficult to filter (an hour and a half was insufficient time to filter all of the slurry at the end of run 22).

Particle size distributions for runs involving low sulphate and high sulphate liquor are shown in Figure 11. The results are only approximate, as the precipitates were filtered, dried, and broken up prior to the measurement of particle sizes. The results do indicate that the jarosite precipitates consisted of larger particles, which is consistent with their superior filterability and handling characteristics.

Impurities in the precipitate are shown in Table 7. Lead is present in amounts up to 0.5 weight %, zinc is generally less than 0.01% of the precipitate, and copper (which is essentially absent from the initial solution) is also very low. Exceptions are run 19 (to which cementation product containing Pb and Cu was added (see the section below)) and run 22, both of which could not be properly washed due to their non-filterability.

SPECIAL TESTS

A chlorinated liquor was used in run 21 to see if the ferric chloride precipitated any faster than the normal ferrous chloride streams. CaO was added as a means of controlling pH. An estimated 25 g/L of iron precipitated in the first hour of operation, which was much more rapid than precipitation in the comparable runs 20 and 21. However, the control of pH

during the run was not successful and the precipitate was very hard to filter. The run was therefore stopped after one hour.

Five grams of a copper-lead cementation product (14% Pb, 15% Cu, 2% Ag) was added to run 19 to observe the effect of copper on the oxidation of ferrous chloride. Although the solution contained 0.3 g/L Cu, the oxidation rate was not materially affected.

Calcium sulphate additions (runs 14 and 20) led to the precipitation of $CaSO_4$ from the cooled liquor samples. Subsequent tests indicated a solubility of 12 g $CaSO_4$ per litre solution at 90°C, but only about 9 g/L $CaSO_4$ at room temperature. Thus the cooling of a liquor stream saturated in $CaSO_4$ resulted in 3 g/L $CaSO_4$ precipitating.

DISCUSSION

The results suggest that the oxidation rate of ferrous chloride is largely unaffected by the subsequent precipitation of iron. Even pH changes due to iron precipitation had little discernable effect on oxidation. As noted by other workers, the partial pressure of oxygen is important. Copper did not appear to have a catalytic effect on oxidation, in contrast to literature results.

Iron precipitation (degree, rates, and products) is strongly affected by rate of oxidation, by the solution pH, and by the presence of sulphate. There are several precipitates that may be obtained, having different filtering characteristics. Iron removal may be affected either by removing about 5 g/L from the whole process stream or by removing 50% or more of the iron from a bleedstream, part of which could be returned to the leaching circuit, the other part exiting the circuit as a bleed stream for maintaining a water balance in the leaching circuit and to control the buildup of impurities. The second option would require the addition of reagents for pH control and would therefore create NaCl or $CaCl_2$. This would reduce the amount of NaCl additions required to maintain the leach solution strength (3 molar NaCl).

$CaCl_2$ addition is being considered as a means of controlling sulphate levels in the leaching circuit. It was shown in this report that $CaSO_4$ addition in the oxidation step would aid in producing a jarosite

precipitate of good handling characteristics while producing $CaCl_2$ as a byproduct. Purchase of $CaCl_2$ would therefore be avoided in lieu of the much cheaper $CaSO_4$.

The precipitation of $CaSO_4$ from saturated liquors that were cooled from 90°C to room temperature may be relevant to the lead chloride crystallization step in the overall flowsheet (Figure 1). Although the solution conditions for the oxidation step are somewhat different from the lead chloride crystallization step, the results suggest that contamination of the lead chloride product by $CaSO_4$ may occur.

In the absence of sulphate, akageneite was precipitated at a pH of 0.5 to 1.0, while an unstable (and difficult to filter) precipitate formed at pH 1.3. Further investigation may be required to determine the lowest pH at which the unstable precipitate forms and to properly identify it. A decision would also be necessary as to the advisability of adding sulphate to the solution in order to obtain a precipitate (jarosite) of good handling characteristics, but which may be environmentally less acceptable than akageneite.

It is interesting to compare the rates of oxididation obtained in this report with those of Rolia and Singbeil (7). They used a fully baffled reactor with a turbine impellor for their experiments. Their impellor speed was 1200 rpm, as compared to 1500 rpm in this report. An oxygen flowrate of 0.60 g O_2/min (0.45 L min^{-1}) was used in their experiments compared to 0.56 g/min in the present study. A comparison of results (by expressing the results of Rolia and Singbeil under the conditions of similar initial ferrous ion concentration and NaCl concentration) is shown in Fig. 12 (which is taken from Fig. 8a). The rates obtained by Rolia and Singbeil (loc. cit.) are clearly greater than those obtained in the present study. Two important factors may have contributed to the difference.

The first important difference between this study and that of Rolia and Singbeil (loc. cit.) was the method of agitation used to disperse oxygen gas in the reactor. The lack of baffling and the use of a marine blade propellor in this report may have led to less than ideal mixing. This is suggested by the results in Fig. 7a, where lower oxygen flowrates led to decreased rates of oxidation, indicating some influence of mass transfer.

Standard engineering practice is to use a turbine impellor and baffling (23).

A second factor that may have contributed to lower rates of oxidation in this report was the low concentration of HCl initially present in the ferrous chloride solutions. Rolia and Singbeil (loc.cit) used a minimum of 0.2 M HCl in their experiments, while only 0.01 to 0.03 M free HCl was present in the feed solutions of this study. This could have had an important effect on the rate of oxidation, as illustrated in Fig. 12, where the results of Rolia and Singbeil (loc.cit) are shown for two different initial concentrations of HCl.

CONCLUSIONS

Ferrous ions can be oxidized and precipitated from the CANMET ferric chloride leach liquor of a New Brunswick complex sulphide ore by contacting the stream with oxygen at 90°C. Up to 15 g/L of iron was removed from the stream after 6 hours without the addition of CaO, up to 44 g/L of iron was removed with the addition of CaO for pH control. The presence or introduction of sulphate in the solution led to the formation of jarosite which was more easily handled and filtered than the other precipitates obtained during the course of experimentation. The precipitates contained only 0.5% lead and 0.01% zinc.

REFERENCES

1. King, D.J. and Acres Davy McKee Engineering Inc. "Ferric chloride leaching of sulfide mineral concentrates Phase I: Final report"; Energy, Mines and Resources Canada, DSS File No. 23SQ.23440-3-9083.

2. Lucas, B.H. and Shimano, D.Y. "Ferric chloride leach process: Progress report"; Division Report MRP/MSL 83-2 (CF); CANMET, Energy, Mines and Resources Canada; 1983.

3. Mathews, C.T. and Robbins, R.G. "The oxidation of aqueous ferrous sulphate solutions by molecular oxygen"; Proc Aust Inst Min Metall 242:p. 47; June 1972.

4. Iwai, M. and Majima, H. "Autoxidation of ferrous ions in a concentrated aqueous solution of ferrous chloride"; Denki Kagaku, 47:12:p. 717; 1979.

5. Iwai, M., Majima, H. "Autooxidation of Fe(II) ions in a spent pickle liquor"; Denki Kagaku 47:11:p. 661; 1979.

6. Posner, A.M. "The kinetics of autoxidation of ferrous ions in concentrated HCl solutions"; Trans Faraday Soc 49:p. 382; 1953.

7. Rolia, E. and Singbeil, B.J. "The oxidation of ferrous chloride: an exploratory study"; Division Report MRP/MSL 83-38 (TR); CANMET, Energy, Mines and Resources Canada; April 1983.

8. Colburn, R.P. and Nicol, M.J. "An investigation into the kinetics and mechanism of the oxidation of iron(II) by oxygen in aqueous chloride solutions"; J Afr Inst Min Metall p. 281; April 1973.

9. Yano, T., Suetaka, T., Umehara, T., Konishi, K. and Horiuchi, A. Nippon Kagaku Kaishi p. 1375; 1974.

10. Pound, J.R. "The oxidation of solutions of ferrous salts"; J Phys Chem 43:p. 97; 1939.

11. George, P. "The oxidation of ferrous perchlorate by molecular oxygen"; J Chem Soc p. 4349; 1954

12. Huffman, R.E. and Davidson, N. "Kinetics of the ferrous iron-oxygen reaction in sulfuric acid solution"; J Am Chem Soc 78:p. 4836; 1956.

13. Majima, H. and Awakura, Y. "Measurement of the activity of electrolytes and the application of activity to hydrometallurgical studies"; Metall Trans B 12B:p. 141; 1981.

14. Ermilov, V.V., Romanteev, Y.P. and Shchurovskii, Y.A. "Oxidation of ferrous chloride by air in a concentrated solution"; Tr Inst Met Obogashch, AkadNaukKaz SSR (Russ.) 30:p. 55; 1969

15. Dutrizac, J.E. and MacDonald, R.J.C. "Ferric ion as a leaching medium"; Miner Sci Eng 6:2:p. 5; April 1974.

16. Dutrizac, J.E. "Recent advances in the leaching of sulphides and in the precipitation of iron"; In press.

17. Kelly, F.J. "Estimated energy requirements for the recovery of hydrochloric acid and the rejection of iron from aqueous solutions containing hydrochloric acid and ferrous chloride"; Division Report MRP/OTT 84-01; CANMET, Energy, Mines and Resources Canada; 1984.

18. Davey, P.I. and Scott, T.R. "Removal of iron from leach liquors by the goethite process"; Hydrometallurgy 2:p. 25; 1976.

19. Boxall, J., Litz, L.M. and Weise, M.K. "A new reactor system for the goethite-zinc leach residue process"; Metallurgical Society AIME paper A84-37.

20. Dutrizac, J.E. "Jarosite formation in chloride media"; Division Report MRP/MSL 80-98 (J); CANMET, Energy, Mines Resources Canada; 1980.

21. Dutrizac, J.E. "Jarosite-type compounds and their application in the metallurgical industry"; Hydrometallurgy Research, Development and Plant Practice 531-551; 1983.

22. Dutrizac, J.E. and Jambor, J.L. "Formation and characterization of argentojarosite and plumbojarosite and their relevance to metallurgical processing"; Proc ICAM '84, Los Angeles; 1984.

23. Perry, R.H., Chilton, C.H. "Chemical Engineers Handbook"; Fifth Edition, McGraw Hill, New York, p. 18-75; 1973.

24. Iwai, M., Majima, H., and Izaki, T. "A kinetic study on the oxidation of ferrous ion with dissolved molecular oxygen"; Denki Kagaku, 47:7:p. 109; 1979.

Table 1a. Oxidation Mechanism
first order with respect to iron(II)
(from Iwai, Majima, & Izaki (24)

Fe^{2+}	+	Cl^-	=	$FeCl^+$			
$FeCl^+$	+	H^+	=	$HFeCl^{++}$			
$HFeCl^{++}$	+	O_2	→	$FeCl^{++}$	+	HO_2	(initiation), rate determining step
$HFeCl^{++}$	+	HO_2	→	$FeCl^{++}$	+	H_2O_2	(propagation)
$HFeCl^{++}$	+	H_2O_2	→	$FeCl^{++}$	+	H_3O_2	(")
$HFeCl^{++}$	+	H_3O_2	→	$FeCl^{++}$	+	$2H_2O$	(termination)

Table 1b. Oxidation Mechanism
second order with respect to iron(II)
(from Colburn & Nicol) (8)

Fe^{++}	+	O_2	=	$Fe^{++}.O_2$				
$Fe^{++}.O_2$	+	Fe^{++}	→	$2Fe^{+++}$	+	$O_2^=$	rate determining step	
H^+	+	$O_2^=$	=	HO_2^-				
HO^{2-}	+	H^+	=	H_2O_2				
Fe^{++}	+	H_2O_2	→	OH	+	OH^-	+	Fe^{+++}
Fe^{++}	+	OH	→	Fe^{+++}	+	OH^-		

TABLE 2. ACTIVITIES OF HCl-NaCl
Aqueous Solutions
(from Majima and Awakura (16))

Activities of HCl in HCl-NaCl Aqueous Solutions at 25°C

HCl	NaCl(mol/l)						
(mol/l)	0.0	0.5	1.0	1.5	2.0	2.5	3.0
0.5	0.0855	0.205	0.358	0.621	0.910	1.48	2.32
1.0	0.808	1.35	2.11	2.96	5.76	9.30	13.7
1.5	1.84	3.45	5.11	7.95	12.7	14.4	26.2
2.0	3.16	6.73	10.8	18.8	26.8	42.3	48.8

Activities of H^+ in HCl-NaCl Aqueous Solutions at 25°C

HCl	NaCl(mol/l)						
(mol/l)	0.0	0.5	1.0	1.5	2.0	2.5	3.0
0.5	0.404	0.468	0.547	0.626	0.738	0.873	1.11
1.0	1.69	1.89	2.06	2.40	2.92	3.70	4.24
1.5	2.88	3.33	3.83	4.54	5.31	5.23	6.35
2.0	4.37	5.14	6.43	7.39	8.57	10.2	9.96
2.5	6.93						
3.0	9.38						
3.5	15.6						
4.0	17.9						

Activities of Cl^- in HCl-NaCl Aqueous Solution at 25°C

HCl	NaCl(mol/l)						
(mol/l)	0.0	0.5	1.0	1.5	2.0	2.5	3.0
0.0		0.316	0.569	0.833	1.17	1.45	1.82
0.5	0.212	0.439	0.655	0.926	1.23	1.69	2.10
1.0	0.480	0.711	1.03	1.24	1.97	2.53	3.23
1.5	0.637	1.04	1.33	1.75	2.39	2.80	4.12
2.0	0.827	1.31	1.68	2.55	3.13	4.15	4.90
3.0	2.32						
4.0	4.46						
5.0	11.0						
6.0	15.0						

Table 3. Precipitates Suitable for Iron Removal (from Davey & Scott (3))

Precipitate	Goethite Akageneite	Jarosite	Hematite
Formula	α & β FeOOH	$RFe_3(SO_3)2(OH)_3$ R= Na+, K+, NH4+	$\alpha - Fe_2O_3$
Temperature (°C)	70-90	90-100	200
pH	2-3.5	1.5	2% H_2SO_4
Anion	Cl^-, $SO_4^=$	$SO_4^=$	$SO_4^=$

Table 4. Commercial Processes for Iron Removal (from Dutrizac (5))

	Cominco	Minemet	USBM	Duval	
Stream Content (g/L)					
$FeCl_2$	50-200		200	4	
CuCl		50	15	20	
NaCl		250	640 (Cl)	80	
KCl				44	
Temperature (°C)	135-165	80	95	104	130
Pressure (atm)	3	1		1	?
pH					?
Residence Time (hrs)				1.5	1.5
Precipitate	Fe_2O_3	β-FeOOH		β-FeOOH K-jarosite	

Table 5. Composition of the Ferrous Chloride Solutions (g/L)

	high (SO_4) solution	low (SO_4) solution
Fe	55	55
Zn	5.2	9.3
Pb	7.5	7.2
Cu	0.3 ppm	1 ppm
Ag	0.2 ppm	0.9 ppm
HCl free	<0.4	<0.4
SO4	9	0.7
Na	64/75	
Cl	195	
Cd		60 ppm
Bi		6 ppm
Ca		0.46
Ba		0.42

Table 6. Experimental Conditions

run #		1	2	3	4	5	6	7	8	10	11	12	13	14	18	19[1]	20	21[2]	22
temperature	°C	80	90	100	90	90	90	90	90	90	90	90	90	90	90	90	90	90	90
gas	O_2/air	O_2	O_2	O_2	air	O_2	O_2	O_2	O_2	O_2	O_2	O_2	air	O_2	O_2	O_2	O_2	O_2	O_2
gas flow	q/min	0.5	0.5	0.5	0.45	0.12	0.56	0.012	0.56	0.56	0.56	0.56	0.56	0.56	0.56	0.56	0.56	0.56	0.56
coal in the feed	q/l	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.59	0.17	0.29	0.0007	0.0007	0.0007	0.0007	0.0007	0.0007	0.0007	0.0007
pH control level															0.5		1.5		1.5
pH adjusting compound															HCL		CaO		CaO
SO_4 adjusting compound										$NaSO_4$	$NaSO_4$	$NaSO_4$		$CaSO_4$			$CaSO_4$		

Special Conditioning

(1) coagulation product added (Cu)
(2) fully carbonated liquor

Runs 9, 17, 16, and 17 are not successful, and are therefore not included in the table.

APPENDIX A

SUMMARY OF DATA

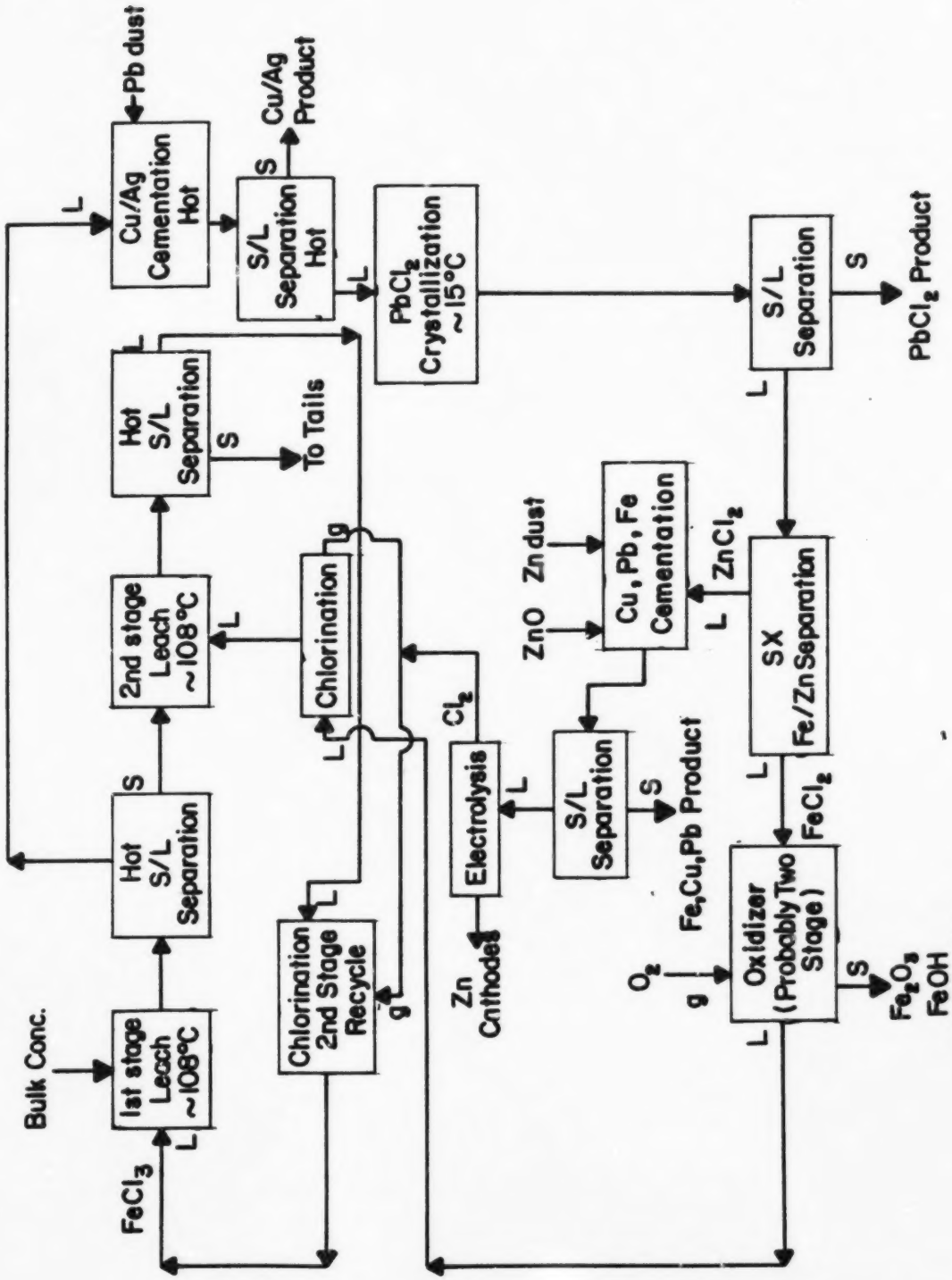


FIGURE 1: PROPOSED TWO-STAGE FERRIC CHLORIDE LEACH PROCESS FLOWSHEET.

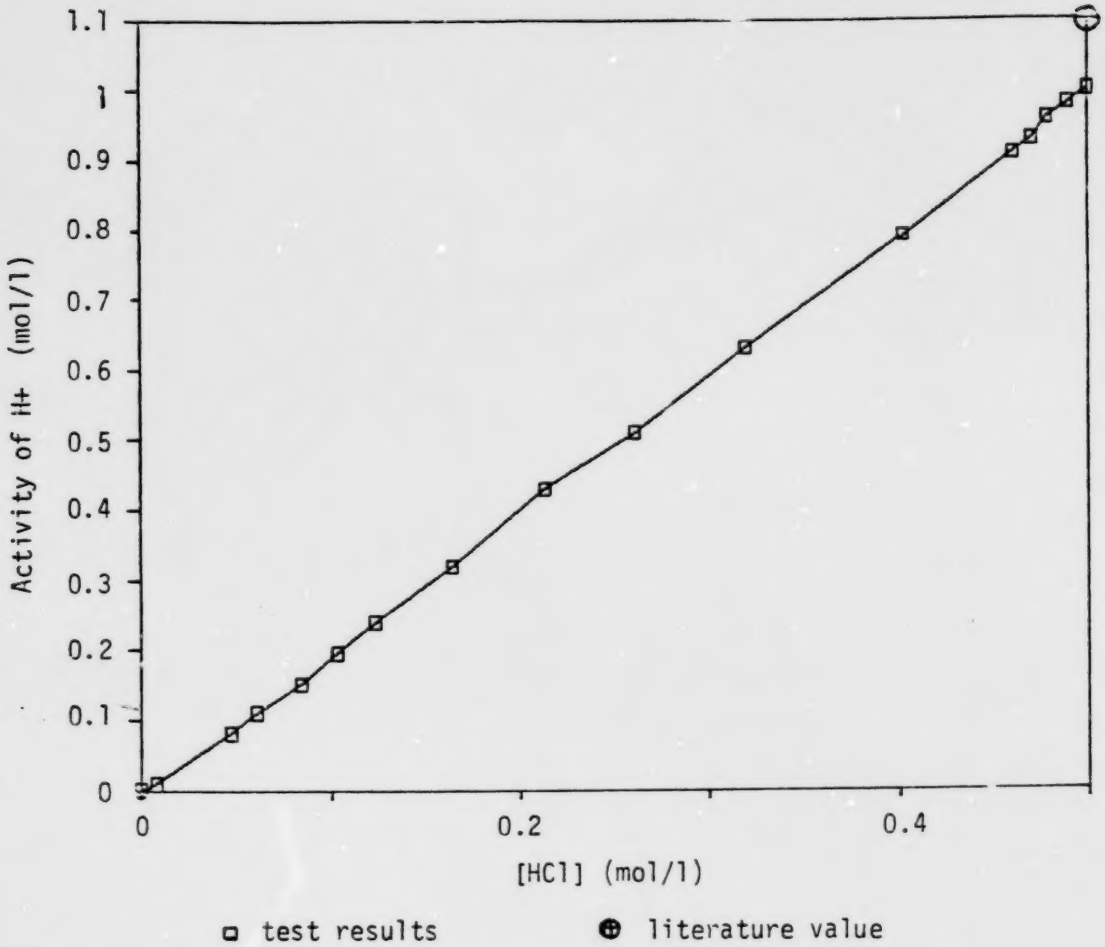


Figure 2. Verification of the pH Probe.

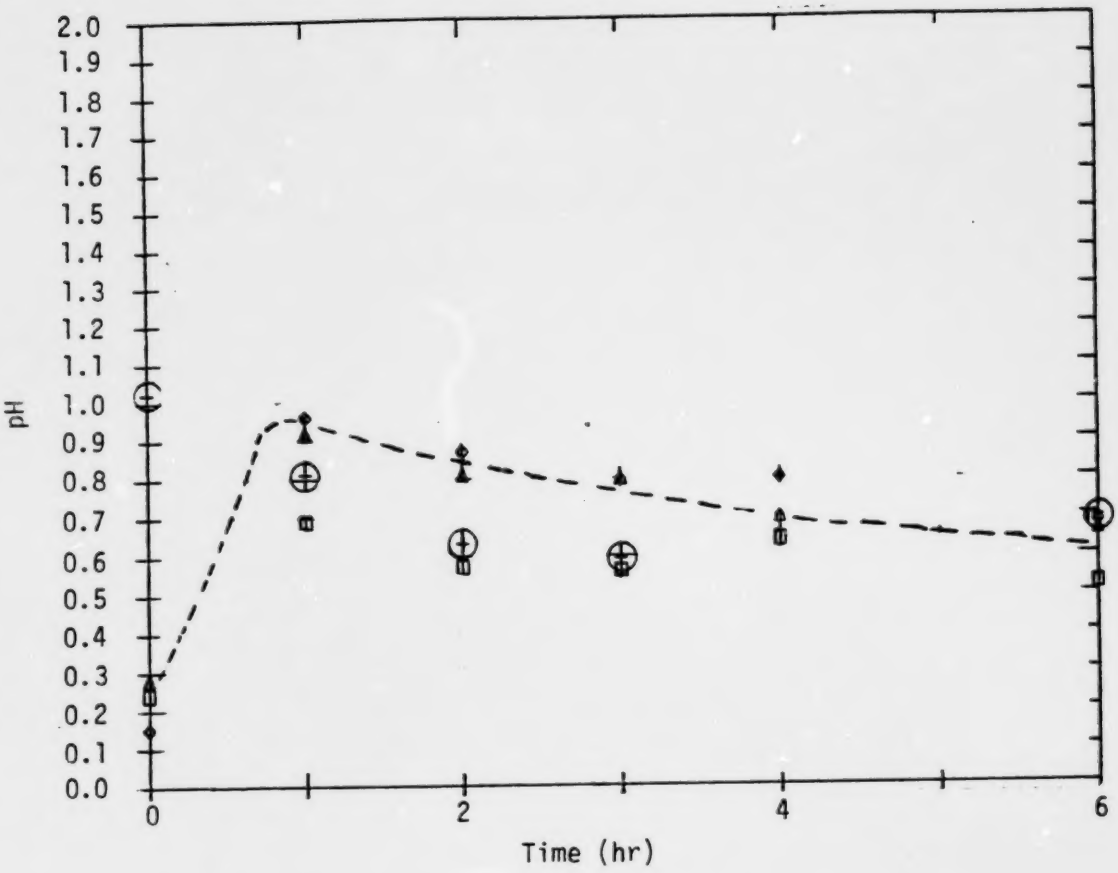


Figure 3. pH Trends with Time.

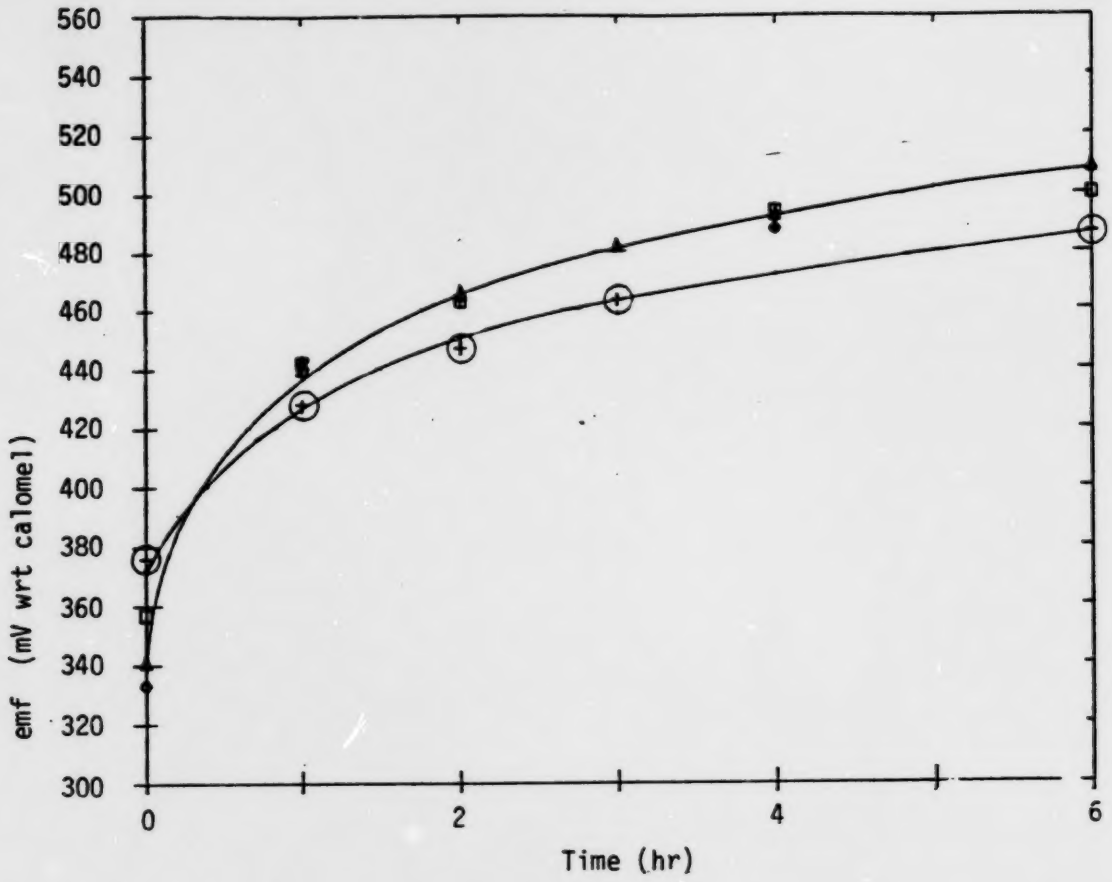


Figure 4. emf Trends with Time.

Symbol	□	⊕	◇	△
Run	2	6	12	15
High/Low Sulfate Liquor	H	H	L	L

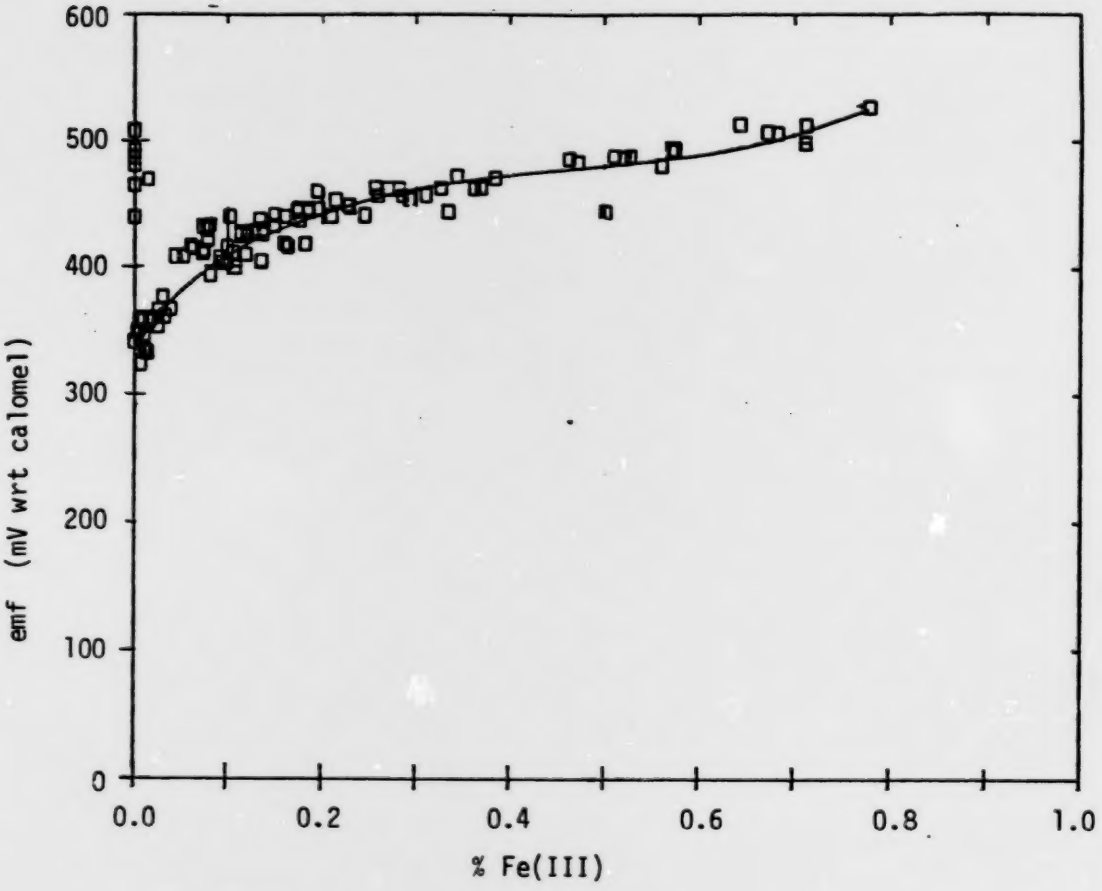
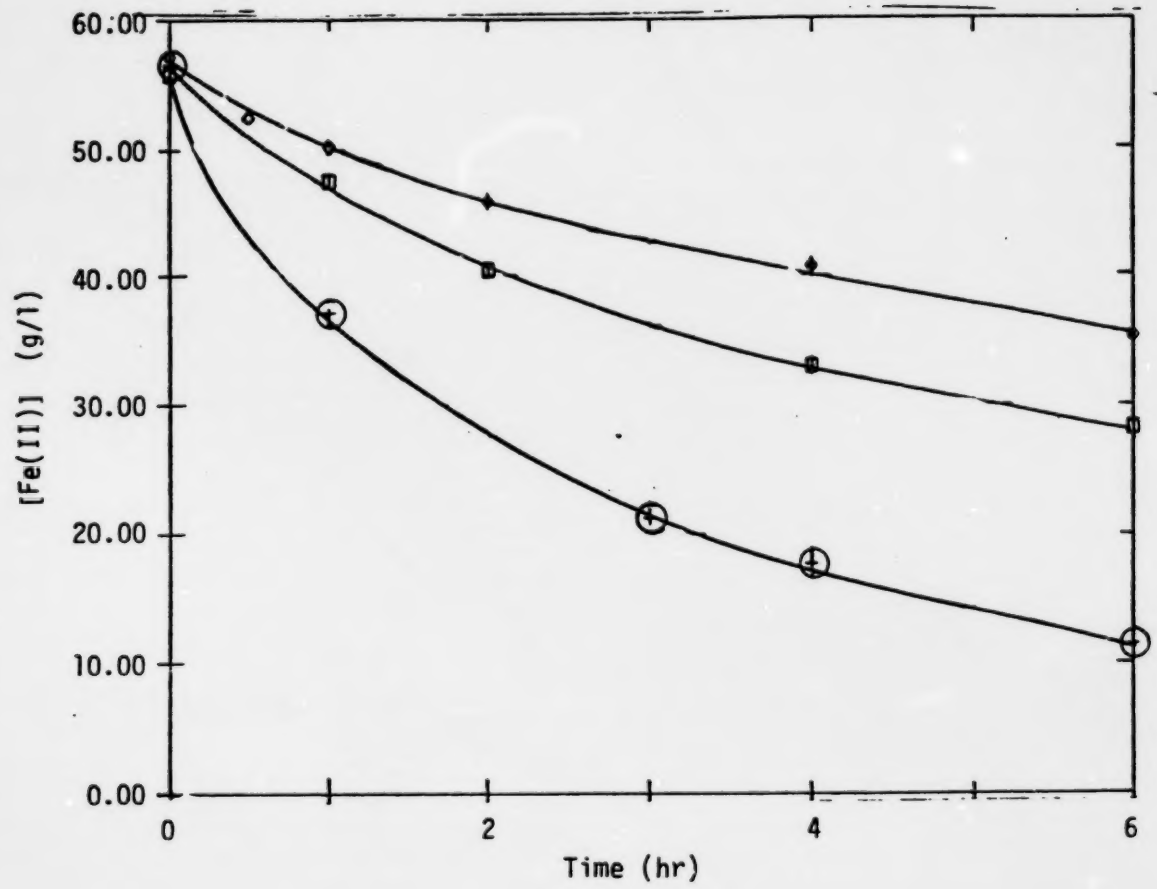


Figure 5. EMF and the Oxidation State of Iron.



Symbol	□	⊕	◊
Run	1	2	3
Temperature (^{o}C)	80	90	100

Figure 6a. The Effect of Temperature on the Oxidation Rate of Ferrous Ion

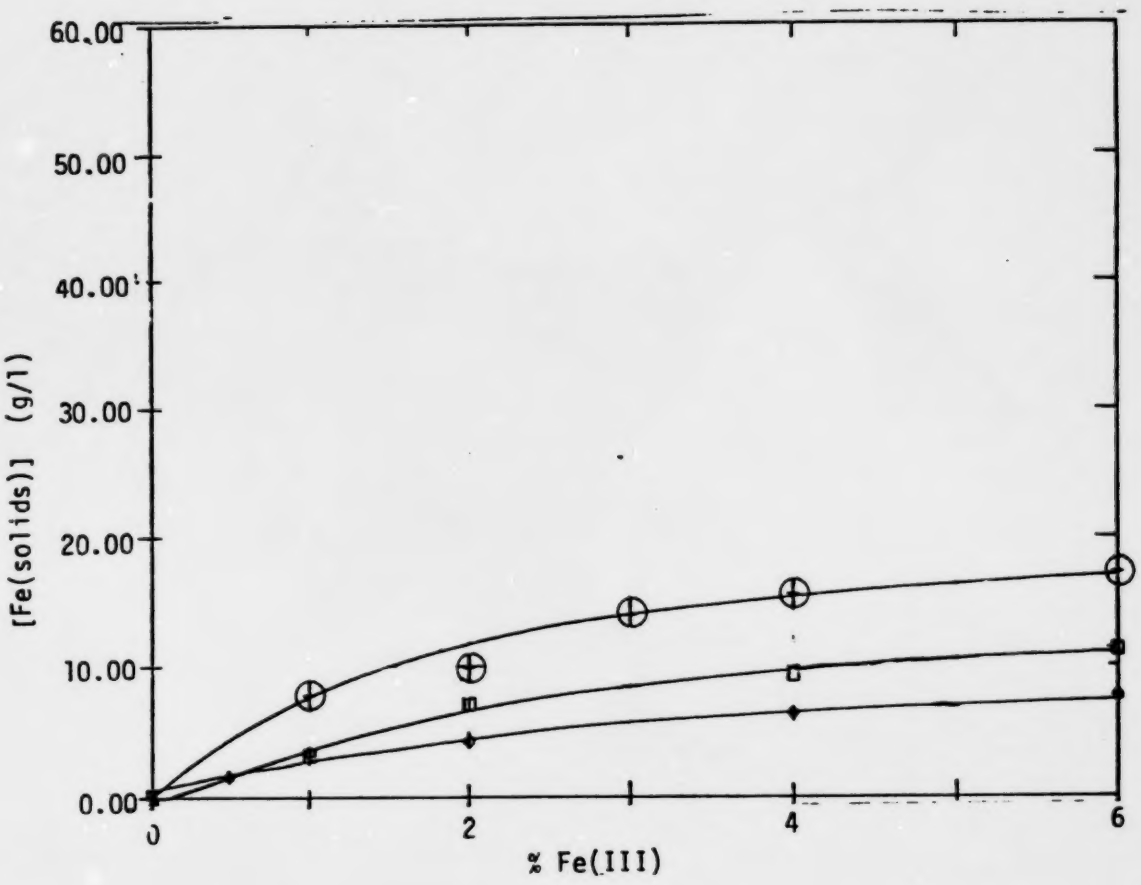
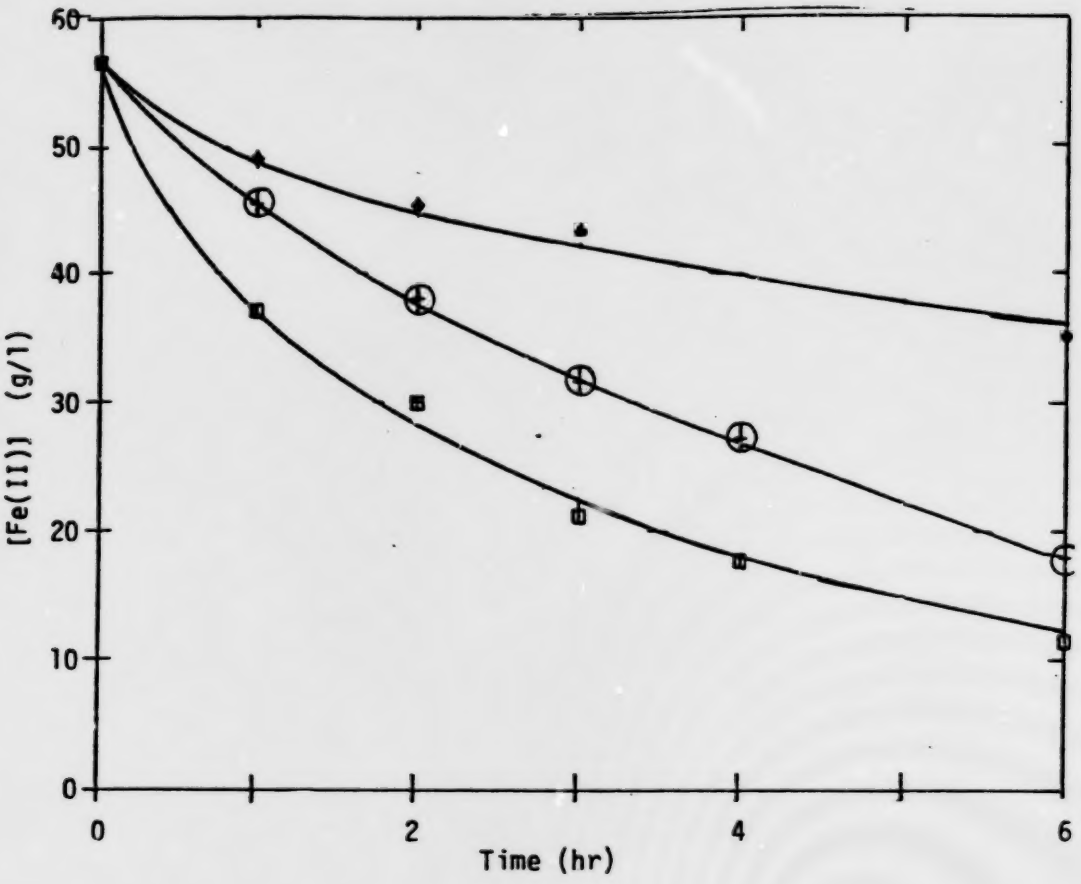


Figure 6b. The Effect of Temperature on the Precipitation Rate of Iron

Symbol	□	⊕	◊
Run	1	2	3
Temperature (^{o}C)	80	90	100



Symbol	□	⊕	◇
Run	6	5	7
O_2 Flow (g/min)	0.56	0.12	0.012

Figure 7a. The Effect of Oxygen Flow Rates on the Oxidation Rate of Ferrous Ion

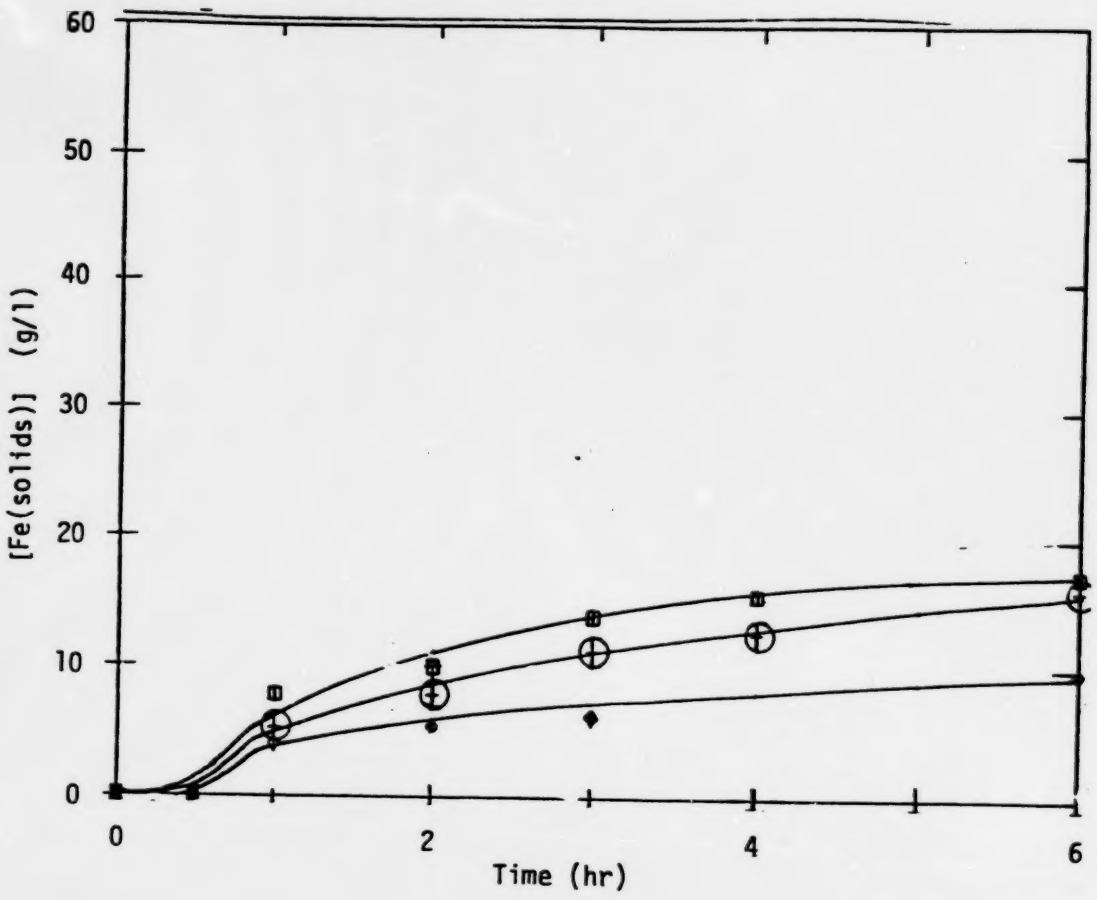
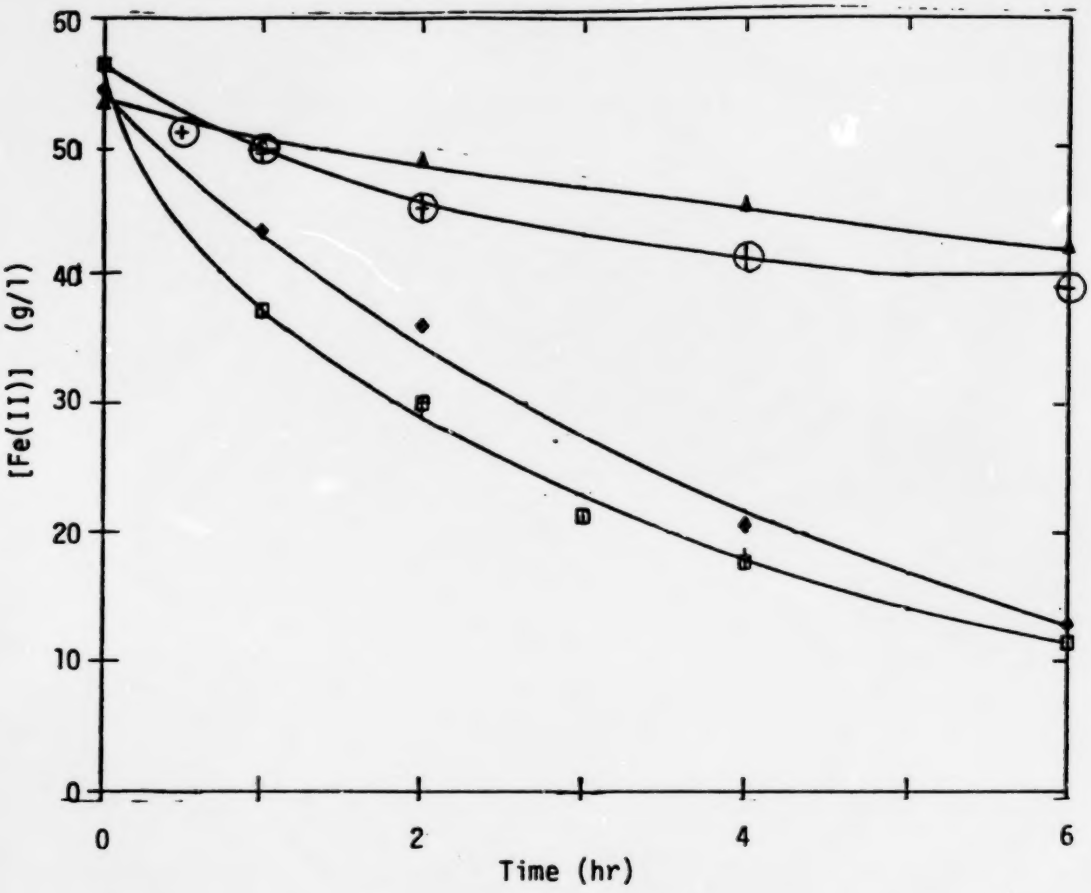


Figure 7b. The Effect of Oxygen Flow Rates on the Precipitation Rate of Iron

Symbol	□	⊕	◇
Run	6	5	7
O_2 Flow (g/min)	0.56	0.12	0.012



Symbol	□	⊕	◇	△
Run	2	4	12	13
Gas	O_2	air	O_2	air
Sulfate (High/Low)	H	H	L	L

Figure 8a. The Effect of Oxygen Partial Pressure on the Oxidation Rate of Ferrous Ion

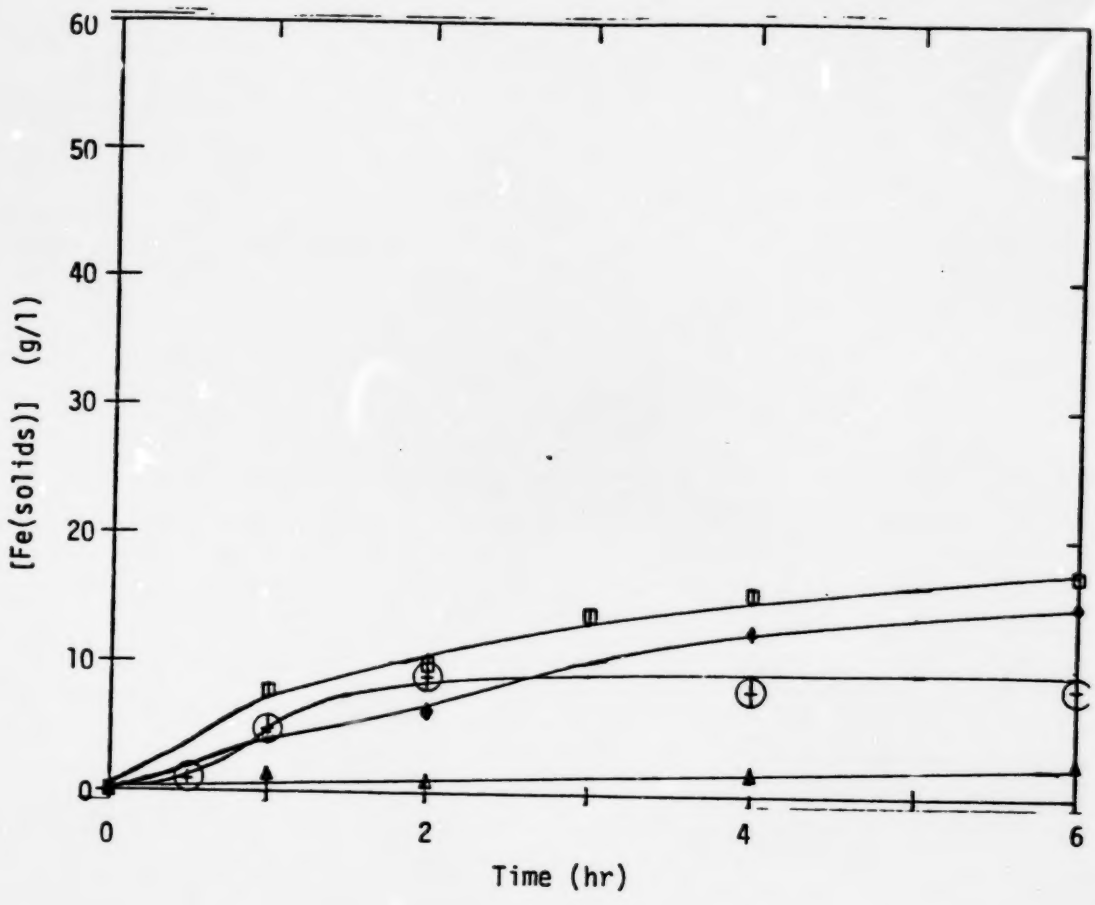
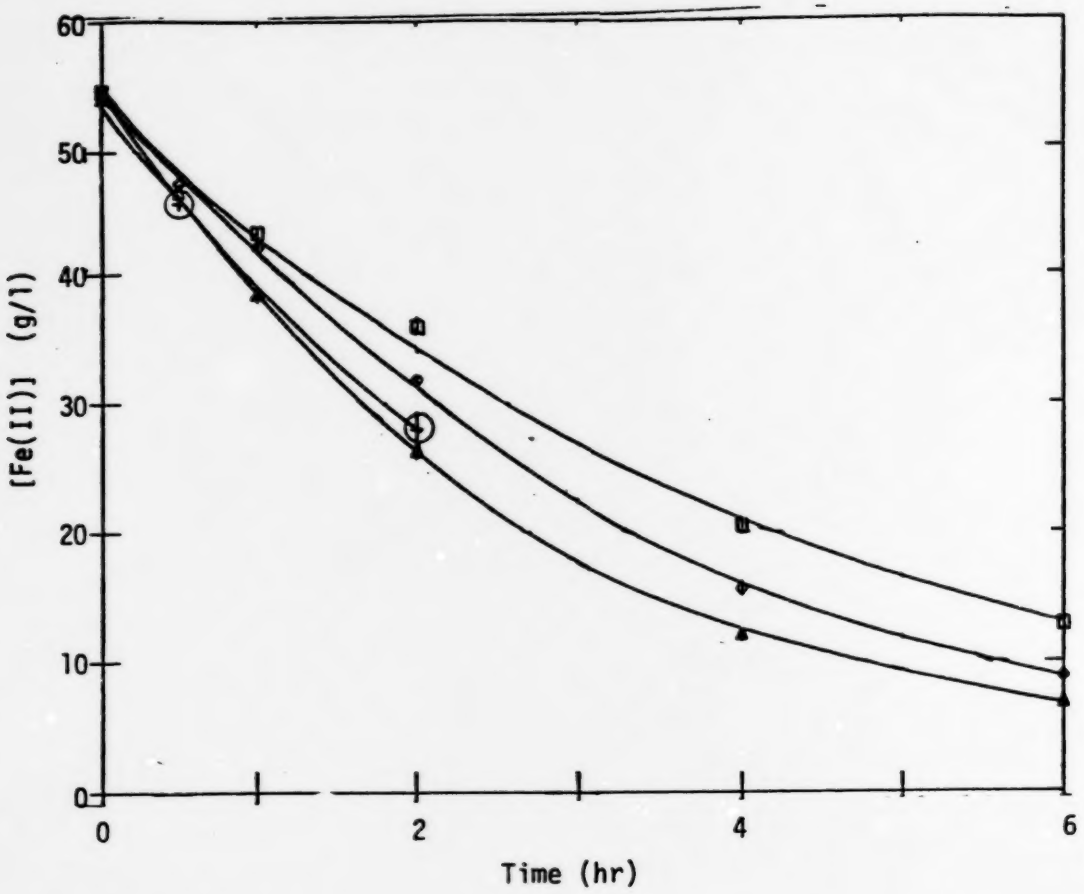


Figure 8b. The Effect of the Oxygen Partial Pressure on the Precipitation Rate of Iron

Symbol	□	⊕	◇	△
Run	2	4	12	13
Gas	O_2	air	O_2	air
Sulfate (High/Low)	H	H	L	L



Symbol	□	⊕	◇	△
Run	12	18	20	22
pH	variable	0.5	1.3	1.3

Figure 9a. The Effect of the pH on the Oxidation Rate of Ferrous Ion

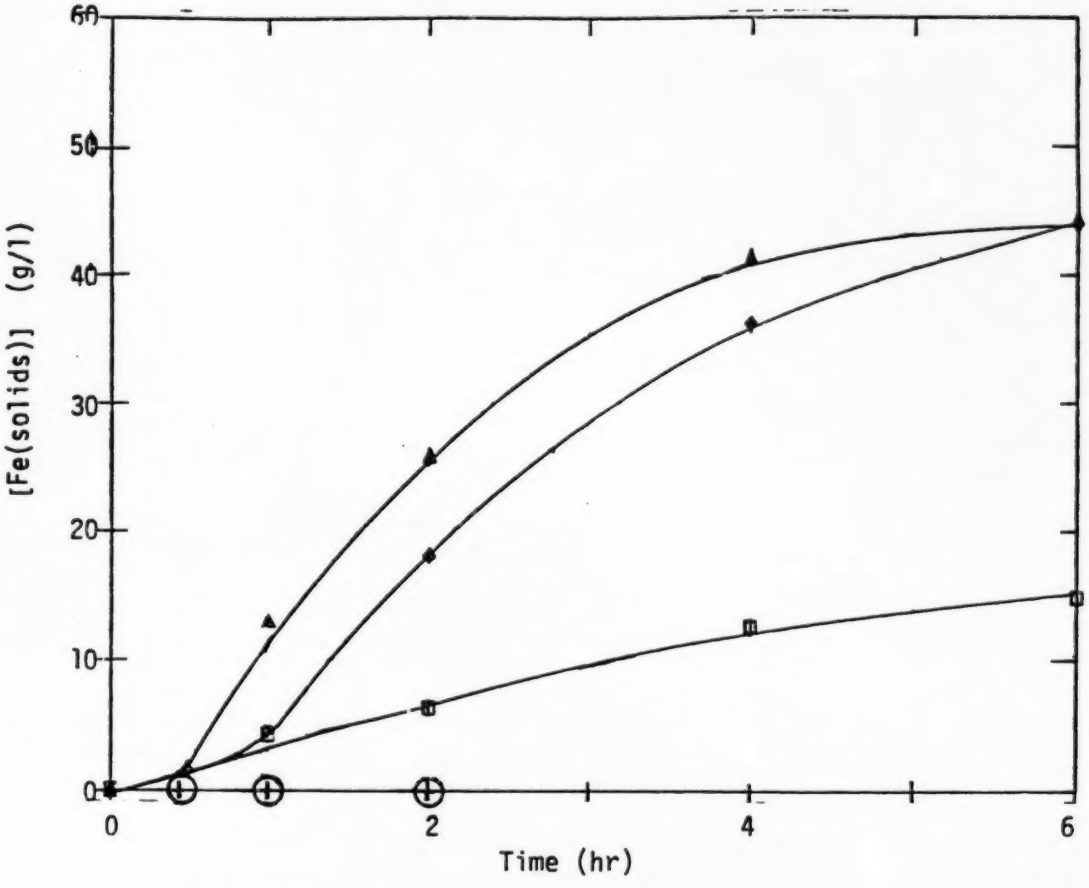
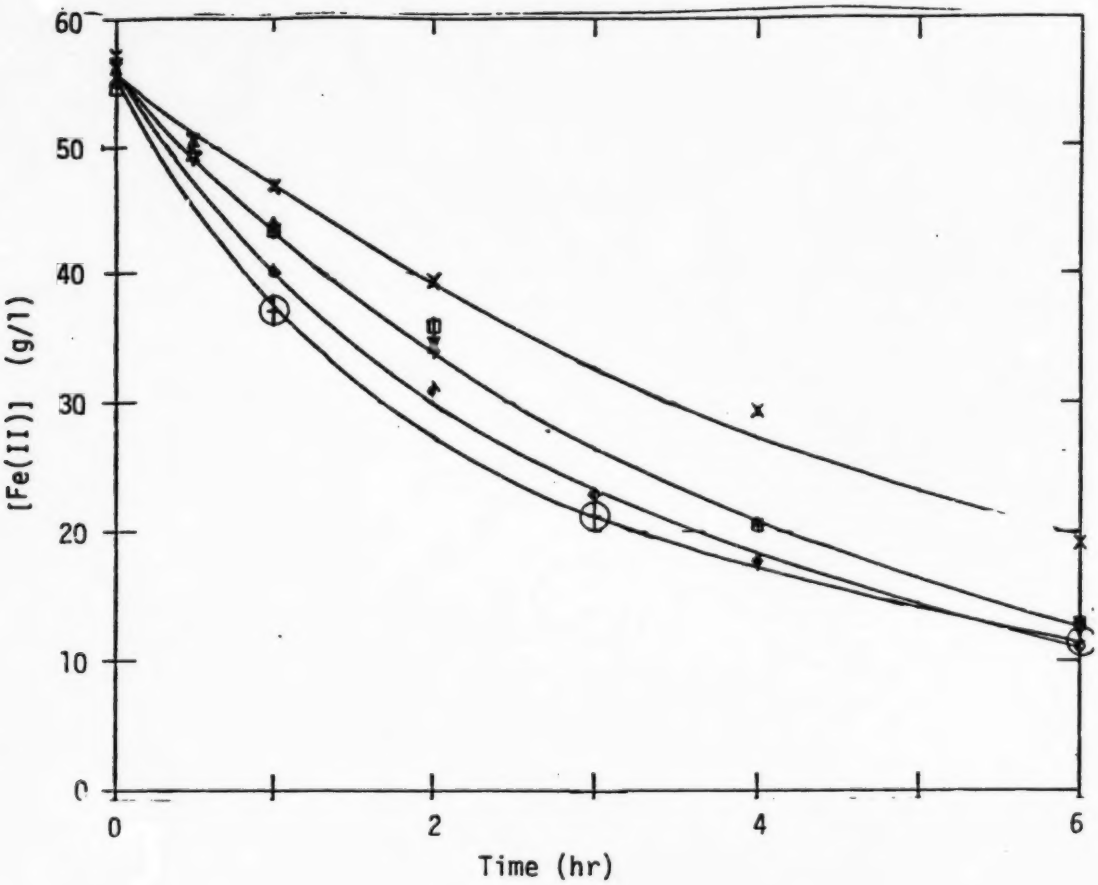


Figure 9b. The Effect of the pH on the Precipitation Rate of Iron

Symbol	□	⊕	◇	△
Run	12	18	20	22
pH	variable	0.5	1.3	1.3



Symbol	□	⊕	◇	△	×	▽
Run	12	2	14	10	11	8
$[SO_4]$ 6 hrs (10^{-2} mol/l)	--	2.50	4.4	0.75	7.77	21.8

Figure 10a. The Effect of Sulphate Levels on the Oxidation Rate of Ferrous Ion

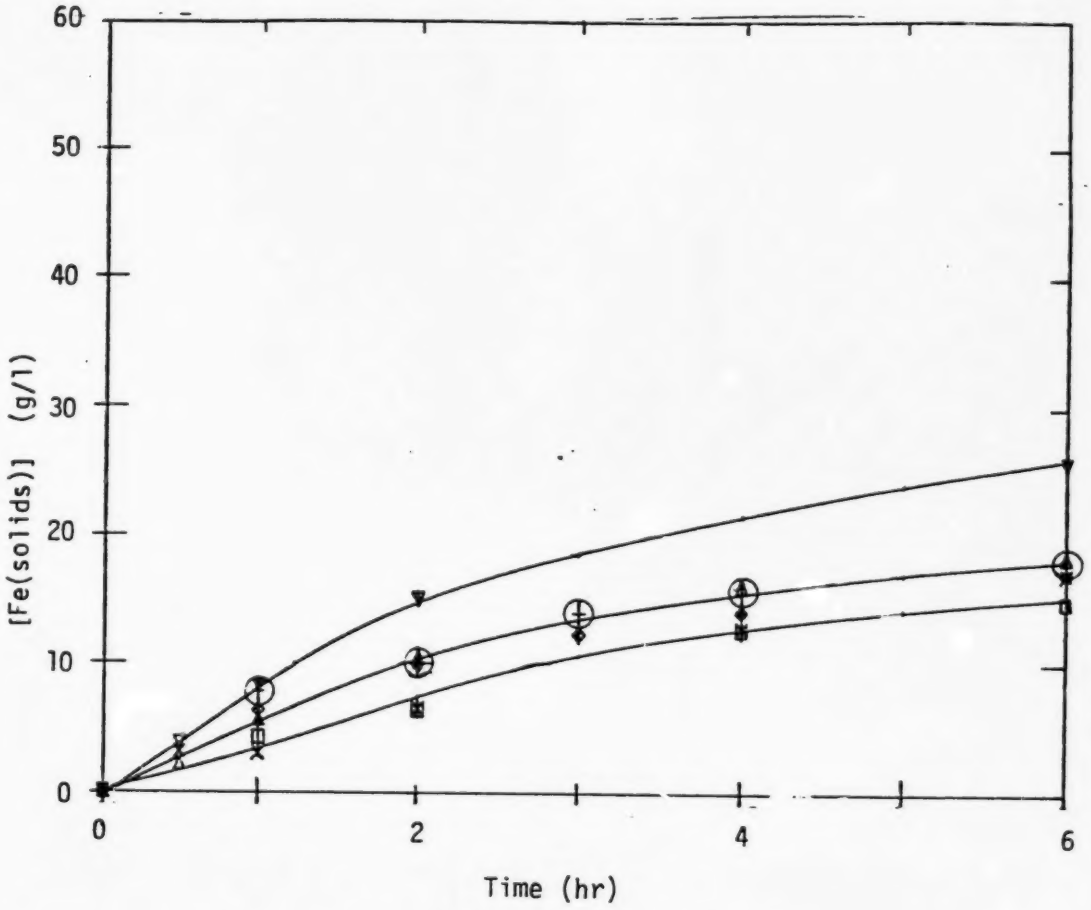
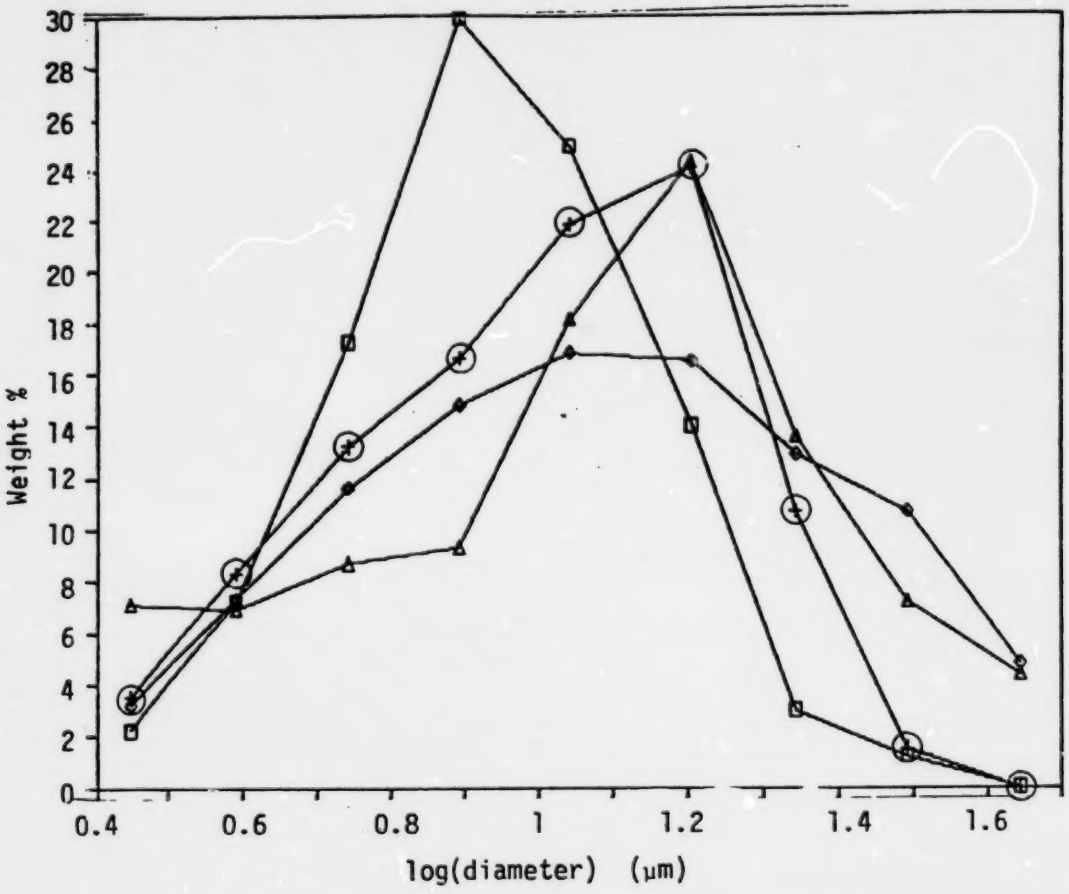


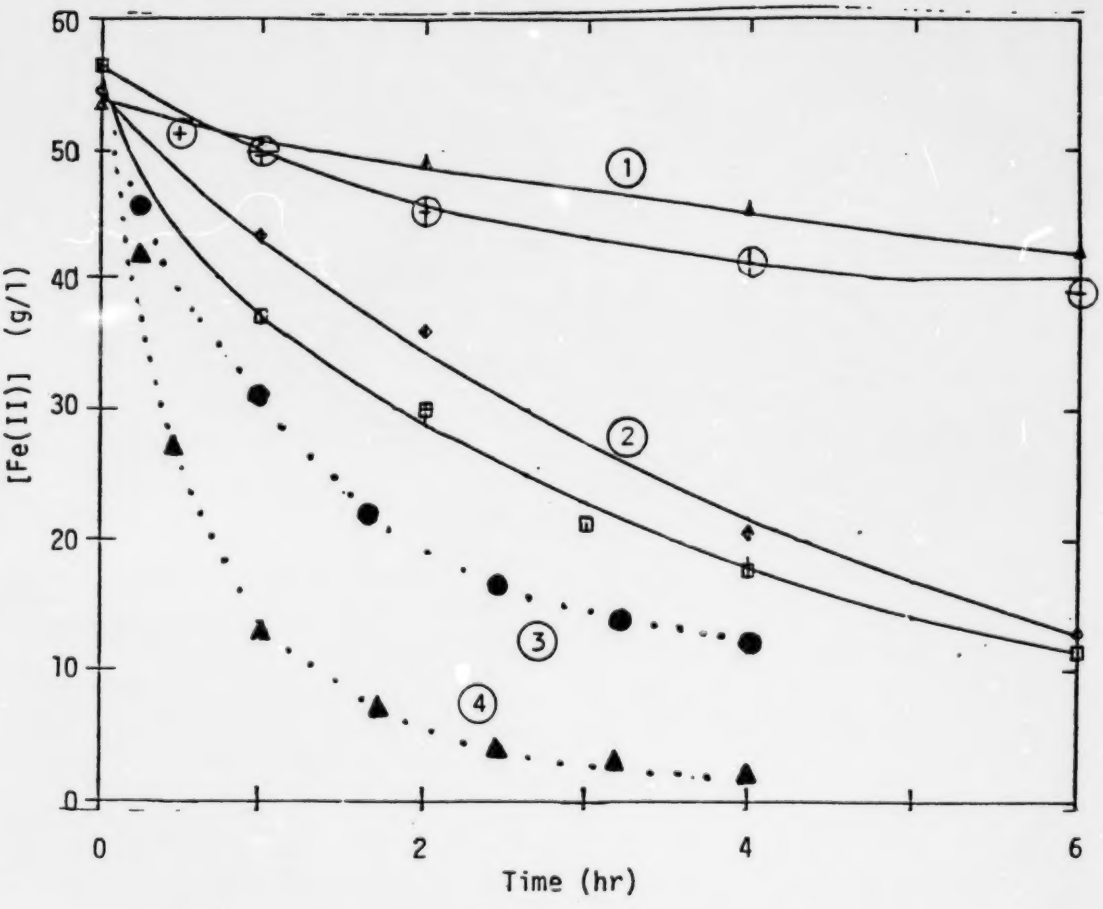
Figure 10b. The Effect of the Sulphate Level on the Precipitation Rate of Iron

Symbol	□	⊕	◇	△	x	▽
Run	12	2	14	10	11	8
$[SO_4]_{6\ hrs}$ (10^{-2} mol/l)	--	2.50	4.4	0.75	7.77	21.8



Symbol	□	⊕	◇	△
Run	12	2	14	8
Feed	low SO_4	high SO_4	low SO_4 $CaSO_4$	high SO_4 Na_2SO_4
$[SO_4]$ average (g/l)	<0.1	5	4.5	40

Figure 11. Particle Size Distribution of the Iron Precipitates



(1)	Howell and Lucas	air	
(2)	Howell and Lucas	O_2	
(3)	Rolia and Singbeil	O_2	0.2 M HCl
(4)	Rolia and Singbeil	O_2	3 M HCl

Fig. 12 A Comparison of the Oxidation Rates Obtained in This Paper With Those of Rolia and Singbeil (7)

Table A1. Summary of Data

RUN #	1	2	3	4	5	6	7	8	10	11	12	13	14	18	19	20	21	22
Time (h)	Ferrous Ion Concentration (g/L)																	
0.00	59.79	56.59	57.19	56.48	56.82	55.99	56.59	56.48	56.50	57.16	54.65	55.72	55.10	54.87	54.55	54.47	n	54.55
0.50	n	n	52.56	51.41	n	n	n	49.21	49.70	50.58	n	n	n	46.00	47.69	47.58	n	46.95
1.00	47.66	57.08	50.55	49.78	45.58	46.52	49.12	45.60	44.20	47.12	45.54	50.60	40.20	38.25	39.65	42.20	1.06	38.54
2.00	40.40	29.95	46.05	45.58	38.02	41.11	45.49	34.62	34.35	39.45	35.90	49.19	30.90	27.92	n	31.79	n	26.41
3.00	n	21.25	n	n	31.56	35.45	45.57	n	n	n	n	n	22.90	n	n	n	n	n
4.00	35.07	17.71	40.50	41.28	27.24	n	n	n	20.57	29.58	20.52	45.65	17.70	n	14.56	15.62	n	12.22
6.00	28.24	11.44	35.50	38.91	17.94	24.86	35.16	12.25	15.02	19.11	12.88	42.15	11.10	n	8.50	8.87	n	6.98
	Ferric Ion Concentration (g/L)																	
0.00	0.54	0.51	-0.11	1.52	0.17	1.75	0.57	2.55	1.95	0.49	0.85	0.58	0.60	0.94	1.46	0.40	68.25	0.66
0.50	n	n	2.98	5.66	n	n	n	5.81	6.58	4.01	n	n	n	7.10	5.44	5.75	n	6.55
1.00	5.26	12.02	5.29	5.46	6.21	5.98	4.05	6.92	8.41	7.50	7.68	2.58	9.20	15.19	9.61	8.04	42.05	5.45
2.00	8.67	17.05	6.81	5.66	11.15	8.75	6.29	9.18	15.45	11.70	15.26	4.25	15.00	25.85	n	4.98	n	2.75
3.00	n	21.77	n	n	14.22	12.22	7.64	n	n	n	n	n	20.50	n	n	n	n	n
4.00	13.68	25.65	9.95	8.67	17.08	n	n	n	21.46	15.45	22.52	7.06	25.90	n	25.89	5.06	n	1.25
6.00	16.62	28.21	14.10	10.61	22.89	21.46	12.27	20.77	26.69	21.40	27.75	9.53	27.50	n	29.90	1.97	n	5.52
	Iron Precipitated from Solution (g/L) (by difference)																	
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.50	n	n	1.54	0.92	n	n	n	5.81	2.17	5.06	n	n	n	2.72	2.86	1.54	n	1.69
1.00	5.20	7.81	5.45	4.75	5.21	5.45	4.01	8.50	5.64	5.05	4.26	1.52	6.50	4.58	6.72	4.65	25.06	15.02
2.00	7.07	9.95	4.25	8.95	7.84	5.89	5.58	15.02	10.47	6.49	6.52	0.88	9.80	4.06	n	18.11	n	25.85
3.00	n	15.90	n	n	11.22	8.07	6.15	n	n	n	n	n	12.50	n	n	n	n	n
4.00	9.58	15.56	6.55	8.04	12.67	n	n	n	16.22	12.82	12.64	1.61	14.10	n	15.74	56.19	n	41.54
6.00	11.21	17.25	7.76	8.47	16.16	9.41	9.75	25.81	18.54	17.14	14.85	2.64	17.10	n	17.60	44.05	n	44.49

n = not available

Table A1. Summary of Data (cont'd)

RUN #	1	2	3	4	5	6	7	8	10	11	12	13	14	18	19	20	21	22
Time (h)	Hydrogen Ion Concentration (g/l)																	
0.00	0.69	0.58	0.58	0.62	0.71	0.10	0.56	0.65	0.59	0.54	0.71	0.42	0.54	1.00	0.58	0.25	n	n
0.50	n	n	0.20	0.25	n	n	n	0.14	0.19	0.19	n	n	n	1.00	0.04	0.04	n	0.06
1.00	0.16	0.20	0.21	0.15	0.20	0.15	0.17	0.28	0.18	0.16	0.11	0.07	0.20	1.00	0.06	0.06	n	0.05
2.00	0.19	0.21	0.51	0.17	0.19	0.25	0.17	0.50	0.24	0.25	0.15	0.08	0.17	1.00	n	0.05	n	0.05
3.00	n	0.28	n	n	0.22	0.26	0.28	n	n	n	n	n	0.18	1.00	n	0.05	n	0.04
4.00	0.22	0.25	0.58	0.55	0.26	n	n	n	0.29	0.47	0.16	0.15	0.20	1.00	0.11	0.05	n	0.05
6.00	0.58	0.50	0.50	0.26	0.71	0.20	0.26	0.89	0.28	0.41	0.21	0.15	0.54	1.00	0.15	0.05	n	0.06
	Sulfate Concentration (mole/liter *100) (1)																	
0.00	9.41	8.04	9.00	9.00	10.28	9.00	9.00	(59.00)	(17.50)	(29.00)	0.07	(0.07)	(4.70)	0.07	0.07	n	8.40	(0.07)
0.50	n	8.04	n	n	n	n	n	(57.55)	(16.78)	n	(0.07)	(0.07)	(4.70)	(0.07)	(0.06)	n	n	(0.06)
1.00	(9.09)	7.56	(7.96)	(8.62)	8.25	(7.90)	(8.45)	(52.15)	(15.97)	(27.98)	(0.06)	(0.07)	5.95	(0.07)	(0.05)	n	0.25	(0.05)
2.00	(7.87)	7.56	(7.52)	(8.12)	8.58	(6.19)	(8.11)	(44.68)	(12.35)	(25.06)	(0.06)	(0.07)	4.57	(0.07)	(0.07)	n	n	(0.02)
3.00	n	6.59	n	n	11.48	(5.70)	(6.75)	n	n	n	n	(0.07)	4.74	(0.07)	(0.07)	n	n	(0.07)
4.00	(6.57)	4.71	(4.29)	(6.25)	4.21	n	n	n	(5.25)	(18.81)	(0.04)	(0.07)	4.90	(0.07)	(0.04)	n	n	(0.07)
6.00	(5.44)	2.50	(1.55)	5.58	1.78	0.75	2.08	21.80	0.69	7.71	(0.05)	0.06	4.40	(0.07)	0.24	0.02	0.05	(0.08)
Element	Precipitate Analysis-final (weight %)																	
Fe	45.80	46.20	58.50	59.40	n	40.50	57.00	55.50	58.80	56.70	52.00	55.00	45.00	n	44.40	50.10	55.60	59.40
S	1.70	0.68	11.15	9.44	n	11.22	11.22	15.50	10.20	11.50	0.05	0.05	6.85	n	0.06	8.75	2.44	0.04
Pb	0.59	0.54	0.45	0.46	n	0.28	0.55	0.47	0.44	0.44	0.52	0.52	0.52	n	0.60	0.12	0.12	0.47
Zn	0.01	0.01	0.01	n	n	n	n	0.01	n	n	n	n	n	n	0.80	0.02	0.22	1.28
Ca	n	n	n	n	n	n	n	n	n	n	n	n	n	n	0.05	n	n	n
Cd	n	n	n	n	n	n	n	6	n	n	n	n	n	n	0.09	8.15	n	5.42

n - not available

(1) - calculated (mass balance) and estimated values of the SO_4 concentration are in parenthesis

Table A1. Summary of Data (cont'd)

RUN #	1	2	3	4	5	6	7	8	10	11	12	13	14	18	19	20	21	22
	Ease of Filterability (2)																	
	G	G	G	G	G	G	G	G	G	G	F	F	G	-	F	G	P	P
	Stability of Precipitate in Water (3)																	
	S	S	S	S	S	S	S	S	S	S	S	S	S	-	U	S	S	U
Time (h)	Rate of Ferrous Oxidation (mol/L/s x 10^5)																	
0.00	4.00	19.70	4.65	4.85	7.08	4.24	4.66	7.14	7.14	5.05	5.58	2.17	8.05	9.67	7.77	6.76	0.00	8.05
0.50	5.85	8.40	5.50	5.75	5.05	5.05	5.76	6.56	6.56	4.96	5.54	1.55	6.58	8.05	7.41	6.57	0.00	7.49
1.00	5.82	5.87	2.62	2.62	4.06	5.08	2.71	5.49	5.49	4.52	5.06	1.15	5.50	6.55	7.41	5.88	0.00	7.05
2.00	2.65	5.55	1.60	1.47	5.22	2.84	1.51	4.55	4.55	5.16	4.28	0.77	4.20	4.11	4.57	4.79	0.00	5.26
5.00	1.68	1.85	1.52	0.91	2.55	2.61	1.08	5.52	5.52	2.51	5.56	0.81	5.51	0.00	5.26	5.89	0.00	5.58
4.00	1.54	1.54	0.80	0.75	2.51	1.78	1.17	2.28	2.28	2.51	2.66	0.86	2.13	0.00	2.06	2.61	0.00	2.12
6.00	1.26	1.55	0.54	0.50	2.51	1.28	1.51	1.47	1.47	2.51	1.52	0.86	1.25	0.00	0.82	0.75	0.00	0.91
	Rate of Iron Precipitation (mol/L/s x 10^5)																	
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.40	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.50	0.00	1.45	0.00	0.00	0.00	0.55	0.50	2.95	0.97	0.46	2.61	1.05	2.88	0.00	5.52	1.59	0.00	4.66
1.00	0.85	1.60	0.29	0.25	0.78	1.07	0.17	5.29	1.50	1.01	0.95	0.17	2.46	0.00	5.18	4.42	0.00	9.05
2.00	0.68	1.55	0.89	0.59	1.45	1.87	0.48	2.54	2.67	1.69	1.55	0.17	1.47	0.00	1.80	7.00	0.00	5.58
5.00	0.51	1.58	0.88	0.61	1.44	-4.21	0.72	1.85	2.09	1.65	1.60	0.17	0.98	0.00	1.14	4.44	0.00	5.82
4.00	0.46	1.02	0.78	0.61	1.06	1.02	0.94	1.55	1.04	1.45	1.04	1.17	0.76	0.00	0.67	2.74	0.00	1.70
6.00	0.44	0.99	0.79	0.61	0.84	0.67	0.61	1.08	0.48	1.55	0.55	0.17	0.75	0.00	0.50	1.61	0.00	0.18

(2) E-Easy, G-Good, P-Poor
(3) S-Stable, U-Unstable